A review of the Tagus river tufa deposits (central Spain): age and palaeoenvironmental record

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A B S T R A C T

Here we determined the aminostratigraphy and aminochronology of tufa deposits located in central Spain associated with the Tagus river and some of its tributaries (the Henares, Dulce, Cifuentes, Ruguilla, Trabaque, Escabas and Guadiela rivers). We used aspartic acid and glutamic acid racemization ratios obtained from the ostracod *Herpetocypris reptans*. Tufa accumulations were found to be of different origins; those in the Henares, Cifuentes and Ruguilla rivers are of paludal origin, while those in the Dulce and Tagus rivers are of fluvial origin. A generally good correspondence was found between the age of the deposits and the position of the terraces above the current thalweg. However, the geomorphological evolution of the Henares, Cifuentes and Ruguilla rivers (infilling of pre-existing valleys) has produced deposits of distinct ages at the same elevation above the current river thalweg, and sometimes, older tufas are located below younger ones.

We distinguished eight main tufa-deposition episodes. These occurred predominantly during even Marine Isotopic Stages (MIS), at 406 ± 90 (MIS 11), 264 ± 68 (MIS 7e), 189 ± 40 (MIS 7a), 130 ± 27 (MIS 6-5e), 101 ± 25 (MIS 5c), 32 ± 10 (MIS 3), 14 ± 4 (MIS 1), and 6 ± 2 (MIS 1) ka. These results are in agreement with the dating of similar deposits from nearby areas and other zones of Spain and Europe. The tufa stable-isotope compositions were similar to other examples in central and southern Spain and their plot falls in the same field as other lowland European stream tufas. Oxygen stable isotopes were influenced mainly by temperature and rainfall. The $\delta^{13}C$ values indicated a major effect of soil-derived carbon rather than carbon from the catchment area, but moderated in each tributary by evaporation, flow regime and biological effects (photosynthesis).

1. Introduction

The term tufa is used in this paper to describe freshwater carbonate deposits developed under ambient temperature conditions (non-hydrothermal) by biomediation and/or physico-chemical processes, as proposed by Pedley (1990), Ford and Pedley (1996), and Pedley et al. (2003). Tufas are characterized by their predominantly low magnesian composition, regardless of crystallinity and high porosity. These deposits sometimes contain abundant plant moulds, often in life orientation. These moulds result from encrustation of the original plant frameworks by fringe cements, thereby producing reef-like barrage constructions (phytoherm frameworks described by Ford and Pedley, 1996). Microbial encrustations are also extensive and commonly manifest as accretionary mammilate to pinnacle-shaped structures around pool margins (stromatolites). Several microbial precipitates are concretionary (oncoids) and can take the form of hollow cylinders when initiated around plant stems (stem encrustation). Pool deposits are generally fine grained (lime muds) towards the depocenters. Phytoclastic sands commonly occur around the pool margins. Sometimes highly organic sapropels and gyttja accumulate in barrage pool systems.

Numerous studies have addressed Pleistocene and Holocene tufa deposits (Virgili and Pérez González, 1970; Ordóñez and González, 1979; Ordóñez et al., 1981, 1987, 1990; Emeis et al., 1987; López Vera, 1989; Pedley, 1990; Chafetz et al., 1991; Andrews et al., 1993, 1994, 1997, 2000; Torres et al., 1994, 1995, 2005; Pentecost, 1995; Ford and Pedley, 1996; Pedley et al., 1996, 2003; Evans, 1999; Arenas et al., 2000, among others). In general, these deposits have been studied from a sedimentological point of view. Traditionally, relative dating has been performed through geomorphological studies. However, the presence of barrages or distinct local-base levels can produce synchronic tufa deposits at a range of relative elevations. Likewise, perched springline tufas and palustrine deposits can develop on top of previous deposits.

Ages can be determined by several dating methods, the most commonly used being ^{14}C and U/Th (Henning et al., 1983; Livnat and Kronfeld, 1985; Blackwell and Schwarcz, 1986; Durán et al., 1988; López Vera and Martínez Goytre, 1988, 1989; Ordóñez et al., 1990; Arenas et al., 2000; Horvatinčić et al., 2000; Garnett et al., 2004; Valero-Garcés et al., 2004). However, the range of the radiocarbon method (*ca.* 30–40 ka) is a serious limitation. U/Th dating presents constraints linked to U-geochemistry (input/output) as well as to detrital thorium (^{232}Th) presence and the method range. In fact, Garnett et al. (2004) observed low U initial concentrations in Holocene tufa deposits together with significant detrital contamination. Moreover, Henning et al. (1983) showed that tufas older than 120 ka display considerable fluctuations in their $^{230}Th/^{234}U$ ratios, probably because these deposits have had greater exposure to post-depositional processes.

Recently, Torres et al. (2005) successfully applied the amino acid racemization method to establish the aminostratigraphy and aminochronology of a tufa system in Priego (central Spain). This method is especially useful for the age range of 10^4–10^6 yr, that is to say, partly beyond the range of the radiocarbon and U/Th techniques. In addition, this method can be applied to a large number of materials, including mollusk and ostracod shells, which are usually abundant in tufa deposits.

Stable isotope data from modern (Andrews et al., 1993, 1997), Holocene/Pleistocene (Andrews et al., 1994, 2000; Arenas et al., 2000; Horvatinčić et al., 2000) and more ancient freshwater carbonates (Zamarreño et al., 1997) record environmental information about water temperature, rainfall (mainly $\delta^{18}O$), vegetation and/or soil respiration (mainly $\delta^{13}C$). Thus, tufas are excellent archives for palaeoenvironmental and palaeoclimatic reconstruction.

With a length of more than 1000 km and stretching from its headwaters in the Iberian Range to its mouth in the Atlantic Ocean, the Tagus river is the longest watercourse in the Iberian Peninsula. In its headwater area and flowing southwest from this Range there are many tributaries with catchments in the same Range. These tributaries flow over mainly carbonate Mesozoic rocks, and have produced considerable tufa accumulations, e.g. the Henares and Dulce rivers, near Sigüenza, and the Cifuentes and Ruguilla rivers, near Trillo (Fig. 1). Likewise, tufa accumulations linked to a small pond in the vicinity of Gárgoles de Arriba have been reported (Fig. 1).

Previous studies of some of these deposits were carried out by Ordóñez et al. (1987, 1990), Benito Calvo et al. (1998), and Pedley et al. (2003). Several attempts to date these materials were made using the radiocarbon method (Gladfelter, 1971, 1972; Preece, 1991) and the U/Th method (Ordóñez et al., 1990; Howell et al., 1995). The studies using the latter, in our opinion, gave controversial results as a result of thorium contamination and, in some cases, uranium leaching, as discussed below. In the present paper we report on the sedimentological study of these tufa deposits together with the amino acid racemization dating of their ostracod valves. Likewise, we performed a palaeoenvironmental reconstruction of these deposits on the basis of their oxygen and carbon stable isotopes signals. To give a general framework of the evolution of the southern part of the Iberian Range during the Middle and Upper Pleistocene and the Holocene, we also examined the amino acid

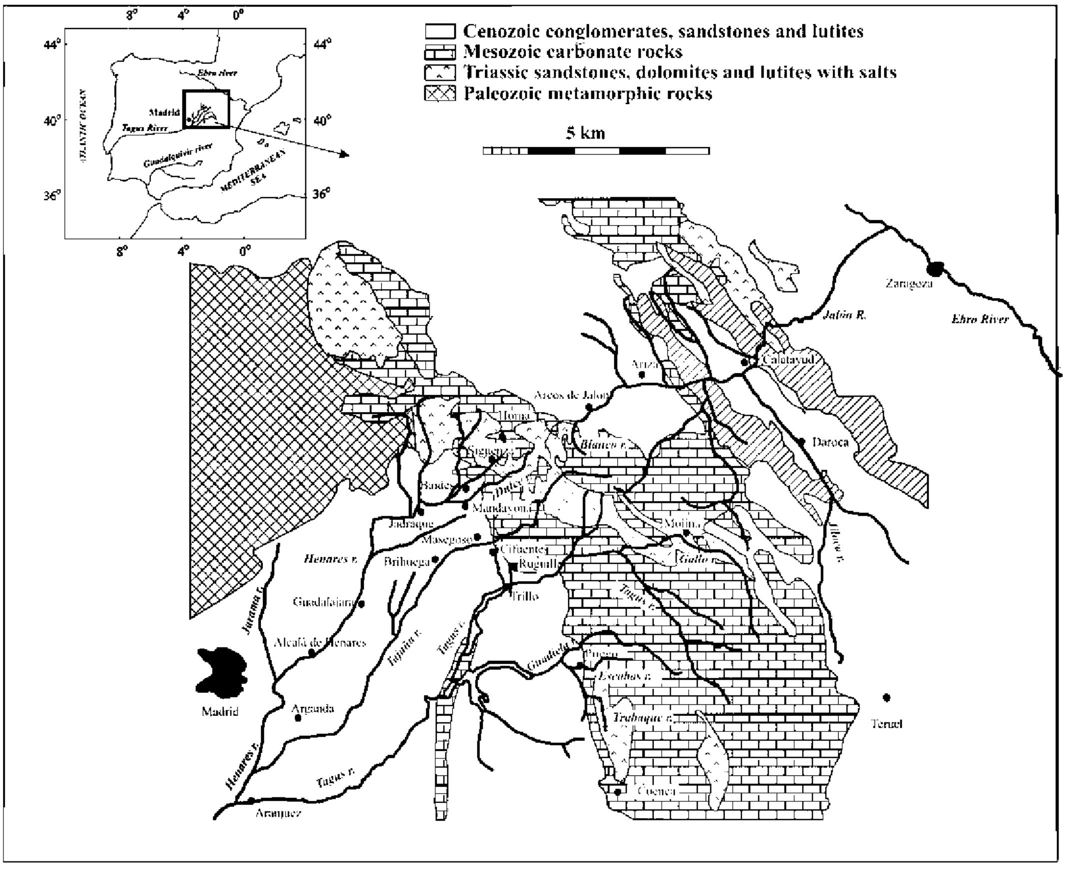

Fig. 1. Geographical location of the study area. The Henares, Dulce, Cifuentes and Ruguilla tributaries of the Tagus river, with their catchment basins in the Iberian Range, which produced tufa accumulations, are shown. The Gárgoles de Arriba lake, which produced tufa accumulations, is also presented.

data from tufa terraces of other tributaries of the Tagus river located in the Priego area, such as the Trabaque, Guadiela, and Escabas rivers (*cf.* Torres et al., 2005), and analysed the stable isotope in these deposits (*cf.* Torres et al., 1995).

2. Geological setting

The Henares river and its tributary, the Dulce river, together with the Cifuentes and Ruguilla rivers, are located in central Spain and belong to the Tagus drainage basin (Fig. 1), which ends in the Atlantic Ocean in Lisbon (Portugal). The Henares and Dulce flow through the Madrid Cainozoic Basin, while the Cifuentes and Ruguilla flow through the *Depresión Intermedia* Basin. The origin of these two basins is related to the Alpine Orogeny. At the end of the Pliocene, erosive processes began, and the current fluvial system was established, thereby producing the development of stepped terrace systems (Torres and Zapata, 1986). The catchment basins of these rivers are in the Iberian Range, which developed during the Alpine Orogeny, and mainly comprises Mesozoic sedimentary carbonates.

Dissolution processes of the carbonate rocks of the drainage areas of the rivers produced $Ca(HCO_3)_2$-rich headwaters which suddenly reached the flat Madrid and *Depresión Intermedia* Basins. The slower flow and development of macrophytes and algae produced CO_2 degassing and consequently the accumulation of tufas.

Downstream of the Henares river, around the village of Sigüenza, fluvial tufa deposits are absent because there is no dissolved calcium bicarbonate available. Tufa deposits reappear around Moratilla de Henares and are linked to a small tributary creek with its catchment area on carbonate Mesozoic rocks. In the vicinity of Baides, tufa accumulations also occur.

Downstream, fluvial terraces comprise extraclastic materials, such as those observed around the cities of Guadalajara and Alcalá de Henares. These materials consist of large accumulations of mainly sands and gravels (Pérez González, 1994). Similar situations occur elsewhere (Violante et al., 1994; Ford and Pedley, 1996) and in other tributaries of the Tagus river, i.e., the Tajuña river (Ordóñez and González, 1979), the Gallo River (López Vera and Martínez Goytre, 1989), and the fluvial system of the Guadiela, Escabas and Trabaque rivers around Priego (Torres et al., 1995).

From our geomorphologic analysis, we identified five terrace levels along the Henares river valley on the basis of their elevation above the current thalweg position (Figs. 2, 3): +50 to 60 m, +30 to 40 m, +15 to 25 m, +10 to 15 m, +3 to 5 m.

Similarly, four terrace levels, located at +55 to 60 m, +20 to 30 m, +10 to 15 m, and +3 to 5 m above the current river thalweg, were distinguished along the Dulce river valley (Figs. 2, 3). In the vicinity of Moratilla de Henares, karsted micritic tufa deposits were detected (MH1.1). These were not correlated with the aforementioned terrace levels because the development of these tufas was related to a small tributary creek.

Tufa deposits of the Cifuentes and Ruguilla rivers are, in most cases, of paludal origin; however, some originated close to karstic springs associated with densely and deeply karsted zones, such as those at the head of the Ruguilla river (*cf.* Ordóñez et al., 1987) and in the pond in Gárgoles de Arriba.

In the Ruguilla river area, two terrace levels were identified (Ordóñez et al., 1987; this paper) (Figs. 3 and 4): the oldest episode of tufa formation was located +50 to 60 m above the current thalweg; the lowest terrace deposits were at +10 to 15 m, although they were poorly represented. Along the Cifuentes river, two tufa-deposition episodes were also observed (Ordóñez et al., 1987; this paper). In this case, the highest terrace (+10 to 20 m) was associated with the stream piracy of the Cifuentes river and was

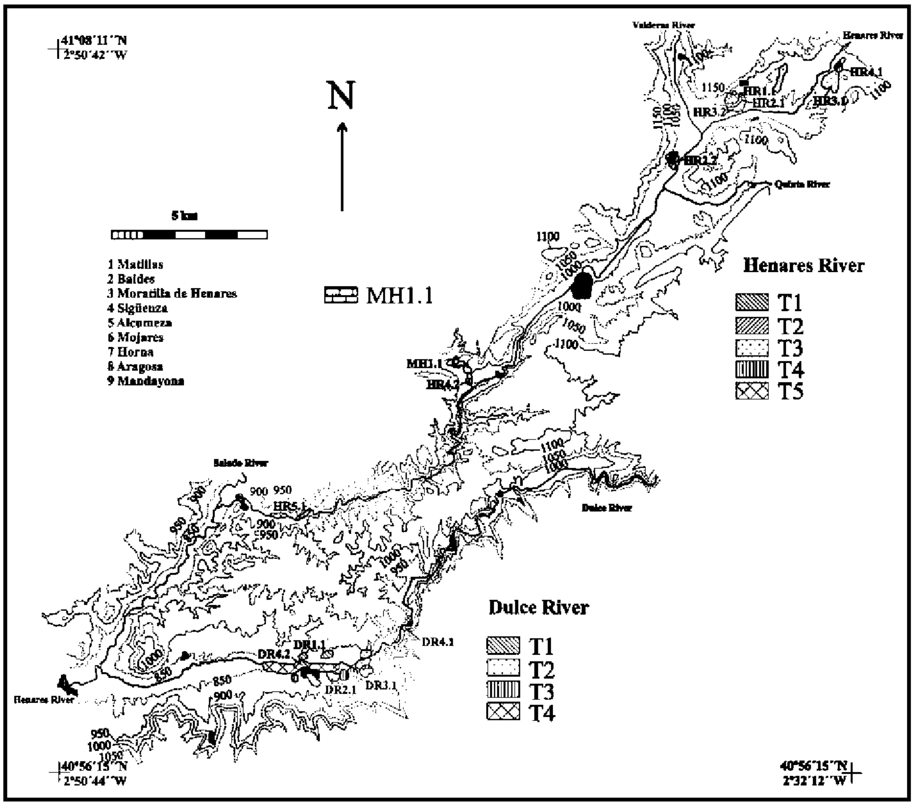

Fig. 2. Map showing the distribution of the tufa fluvial terraces of the Henares (HR) and Dulce (DR) rivers on the basis of their relative elevation over the current thalweg (5 terrace levels for the Henares river and 4 for the Dulce river, being 1 the highest) and the downstream order. T: terrace level.

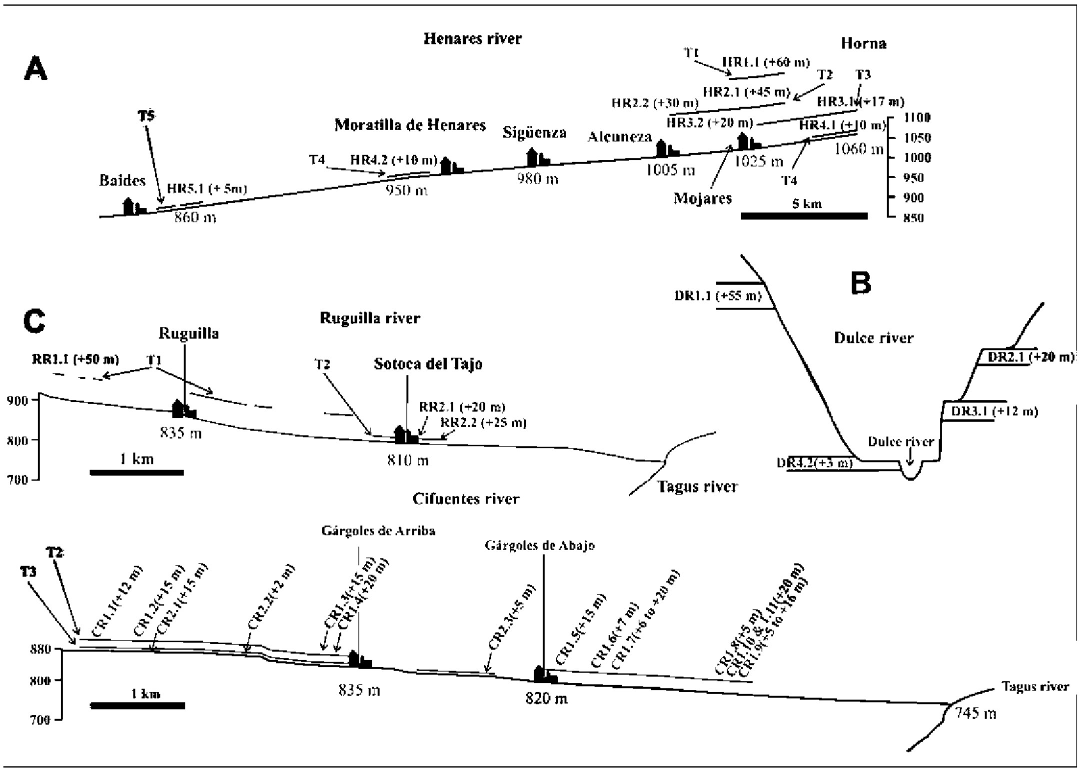

Fig. 3. Cross-section profiles (longitudinal profiles) of the Henares, Dulce, Ruguilla and Cifuentes rivers showing the tufa terrace levels. Each section was identified on the basis of the related river (Henares river-HR; Dulce river-DR; Ruguilla river-RR; Cifuentes river-CR), its geomorphological situation on the basis of the elevation above the current thalweg (5 terrace levels for the Henares river, 4 for the Dulce river; 3 for the Cifuentes and Ruguilla rivers – the highest terrace of the Cifuentes river can be correlated with the lowest terrace deposits of the Ruguilla river) and the downstream order along the river longitudinal profile. T: terrace level.

correlated with the lowest terrace deposits of the Ruguilla river; the sub-recent episode of tufa deposits was located at +3 to 5 m.

The Gárgoles de Arriba pond occurs in a small depression developed over Miocene deposits fed by karstic springs on Mesozoic carbonate rocks, thereby producing large tufa deposits (Figs. 3 and 4).

Two terraces were observed along the Tagus near the mouth of its tributaries (Cifuentes and Ruguilla Rivers). The tufa deposits sampled from the Tagus were +25, and +8 to +5 m above the current thalweg (Figs. 3 and 4).

2.1. Sedimentological description

Several classifications of tufa deposits have been proposed elsewhere (e.g. Symoens et al., 1951; Geurts, 1976; Buccino et al., 1978; Ordoñez and García del Cura, 1983; Chafetz and Folk, 1984; Pentecost and Lord, 1988). In the present study a mixture of "paleogeomorphological" (paleoenvironmental analysis) and sedimentological criteria were used, following those proposed by Pedley (1990) and later reviewed by Ford and Pedley (1996). There are four main environmental models in which most tufa deposits occur: fluviatile, perched springline, lacustrine and paludal. We distinguished twelve types of tufa and associated deposits (Table 1), following Pedley (1990).

For facies description we selected diverse representative sections (see Figs. 5 and 6; for location, Figs. 2 and 4) in which the distinct types of deposits were identified. Each section was referred to on the basis of its associated river (Henares River-HR; Dulce River-DR, Cifuentes river-CR; Ruguilla river-RR; Tagus river-TAR), the relative elevation over the current thalweg (e.g. T1–T5 for the Henares river, being T1 the highest and T5 the lowest terrace levels, respectively) and the downstream order (Fig. 2). As an example, HR4.2 refers to the second (2) downstream section analysed of the 4th terrace level (T4) of the Henares river. Sections related to the activity of the Gárgoles de Arriba lake are named GP.

The tufa deposits of the Henares and Dulce rivers fell in the framework of Pedley's (1990) fluviatile–paludal model, while the tufas of the Cifuentes and Ruguilla rivers were found to be mostly of paludal origin. Lacustrine–paludal type tufas (Gârgoles de Arriba lake) and fluviatile ones (Tagus river) were also found.

The fluviatile model, which includes braided and barrage submodels (Pedley, 1990; Pedley et al., 1996), consists of a network of small channels, which join and separate repeatedly around bars (Miall, 1977) made of intraclasts, extraclasts or bioherms (Phytoherms). In the study area, fluviatile tufas are usually associated with mostly braided channels, where extraclast input may be temporarily dominant. In the braided sub-model (Pedley, 1990; Pedley et al., 1996), oncoliths (cylindrical and spherical) predominate in shallow rivers. Erosive bases and fining upwards beds occur. Ripple lamination is frequent and phytoclasts are very common. Stromatolite domes have developed on stabilized substrates in channels or on channel margins.

Paludal tufas usually form on low-gradient and valley-floor sites, with very shallow water (less than 10 cm deep). Sometimes, in the last stages of valley infilling, fluviatile tufas can be succeeded by paludal tufas. According to Pedley (1990), Ford and Pedley (1996), and Pedley et al. (2003), given the slow water flow, paludal tufas do not contain transverse phytoherms barrages, only small phytoherm cushions can occur, and spheroidal cyanoliths (oncolites) are rare or absent. Hydrophytic macrophytes (mostly *Sparganium* and *Typha*) encrusted by fringe cements (only the plant stems below water become coated) are common in the central parts, while in the marginal zones grass tussocks and bryophyte hummocks may predominate. Lime mud is common and gyttja

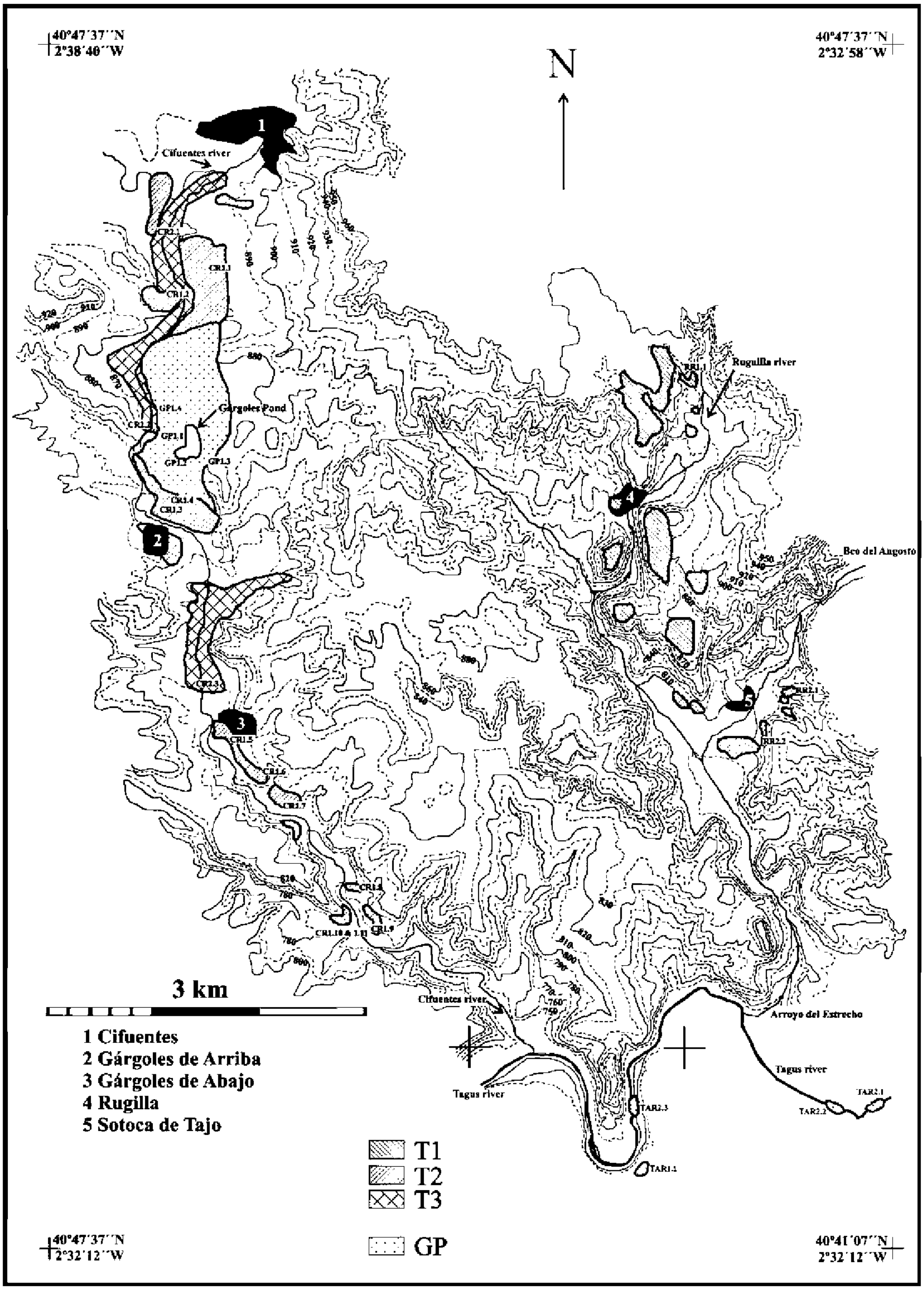

Fig. 4. Map showing the distribution of tufa fluvial terraces of the Cifuentes (CR), Ruguilla (RR) and Tagus (TAR) rivers on the basis of the relative elevation of these terraces over the current thalweg and geographical location of the stratigraphic sections examined. Tufa deposits from Gárgoles de Arriba lake (GP) are also shown.

accumulations can be found. Wetland pulmonate gastropods predominate.

Lacustrine tufas (*cf.* Pedley, 1990; Pedley et al., 1996) are associated with large static bodies of freshwater. Macro- and microphytes are common in littoral shallow zones, together with *Chara* stems, stromatolites (algal bioherms) and oncoliths. Intraclasts, bioclastic sands, mainly composed by phytoclasts and shells, are abundant. Lime mud is abundant and covers much of the lake floor. Fauna is diverse, including mollusks and ostracods, among others.

In many sections of the Henares and Dulce rivers gravels/conglomerates are found (DR1.1, DR2.1, DR3.1, M61, HR3.1, HR5.1; Fig. 3), together with oncoliths (HR3.1, DR4.1, MH1.1). These observations indicate a fluviatile origin with episodes of increasing energy. However, these sections end with lime mud precipitates

Table 1
Facies of tufa and associated deposits distinguished in the area of Priego.

Autochtonous deposits	Clastic deposits	Other deposits
Phytoherm framestone tufa (Pht)	Phytoclastic tufa (Pct)	Paleosols s.l. (Pls)
Phytoherm boundstone tufa (Pbt)	Oncolitic tufa (Ont)	Karst deposits (K)
	Intraclastic tufa (Int)	Extraclastic deposits (Ecl)
	Micritic tufa (Mct)	Gytja and sapropel deposits (Gyd)
	Peloidal tufa (Plt)	

with horizontal lamination, phytoherm boundstone and framestone (*Sparganium* and *Typha*) tufas and, in some cases, stromatolites (grass tussocks and bryophyte hummocks), thereby suggesting lower energy associated with a paludal origin.

Stratigraphic sections of the Ruguilla and Cifuentes rivers consist mainly of phytoherm boundstone and framestone tufas and, to a lesser extent, intraclastic silts and sands. There is no evidence of high energy deposits.

The Gárgoles de Arriba lake deposits are made of calcareous silts with abundant gastropod and ostracods interbedded with phytoherm framestone tufas of *Chara*.

Tagus river sections consist mainly of extraclastic sands and gravels, with high-scale epsilon cross bedding (in TAR1.1). Sometimes lutites and sapropels (peaty lutite) appear.

3. Material and methods

Material recovered was used for amino acid racemization analysis in the Laboratory of Biomolecular Stratigraphy (E.T.S.I.Minas Madrid) and for carbon and oxygen stable isotope determination in the *Laboratorio de Isótopos Estables* (E.E. El Zaidín).

3.1. Amino acid racemization analysis

Samples were taken from beds comprising marls or silt. In all cases, a 1-m deep hole was dug before collecting a 3-kg sample. In the laboratory, the samples were washed and sieved. After drying, the sediment remnant (>0.062 mm) was analysed under a binocular microscope and ostracod caparaces were picked up with the aid of a needle. Ostracod shells were carefully cleaned sonically and with water to remove sediment. Only translucent individuals were selected for the analysis.

Ostracod shells from different genera, including mainly *Candona* and *Ilyocypris* valves, were recovered in 40 sampled sections,

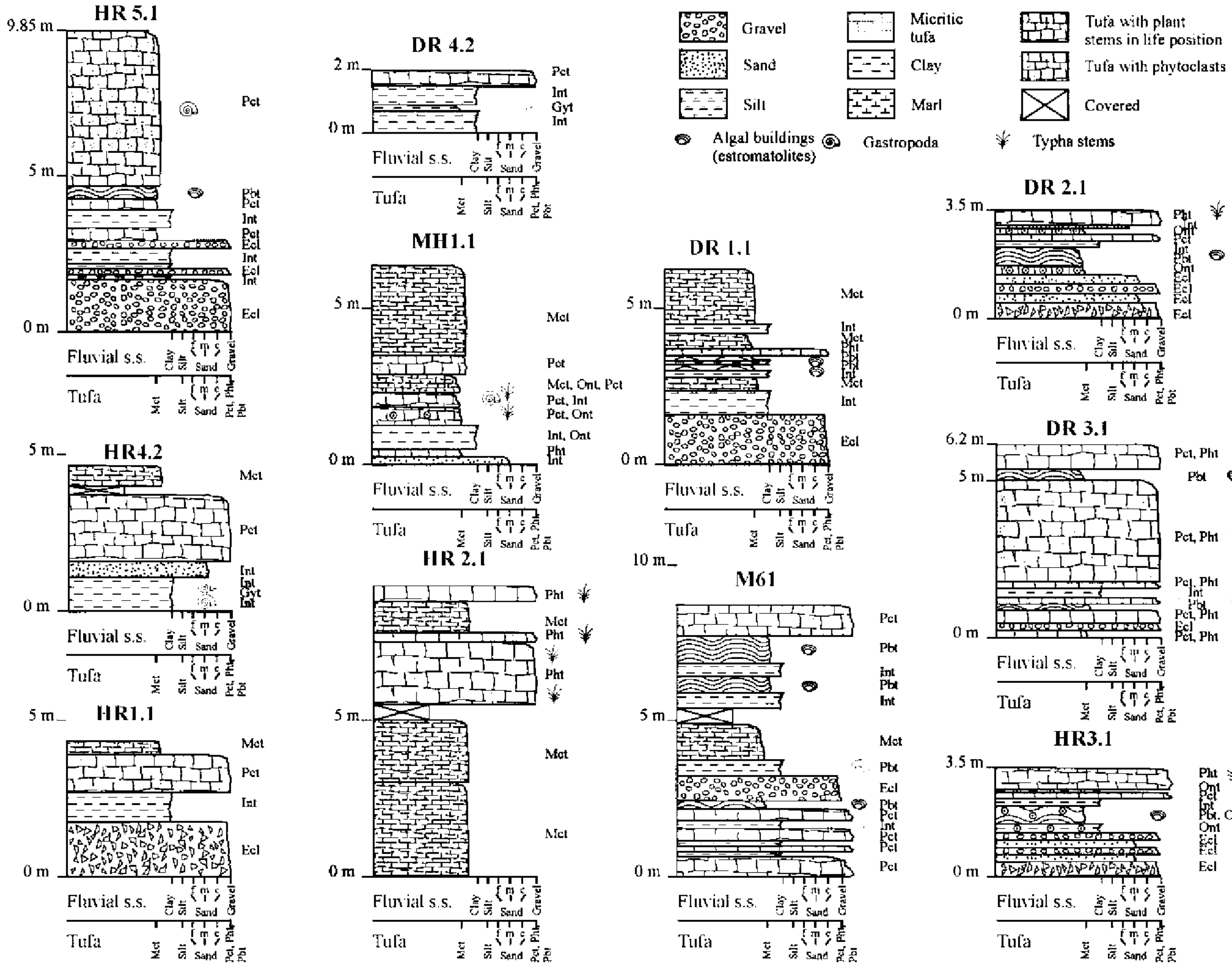

Fig. 5. Several representative stratigraphic sections of the Henares and Dulce rivers with the facies identified. Location of the samples (S) is shown in each stratigraphic section. Tufa facies (Pedley, 1990) are also shown; Autochtonous deposits: Phytoherm framestone tufa (Pht), Phytoherm boundstone tufa (Pbt); Clastic deposits: Phytoclastic tufa (Pct), Oncolithic tufa (Ont), Intraclastic tufa (Int), Micritic tufa (Mct); Other deposits: Karst deposits (K), Extraclastic deposits (Ecl), Gyttja and sapropel deposits (Gyd).

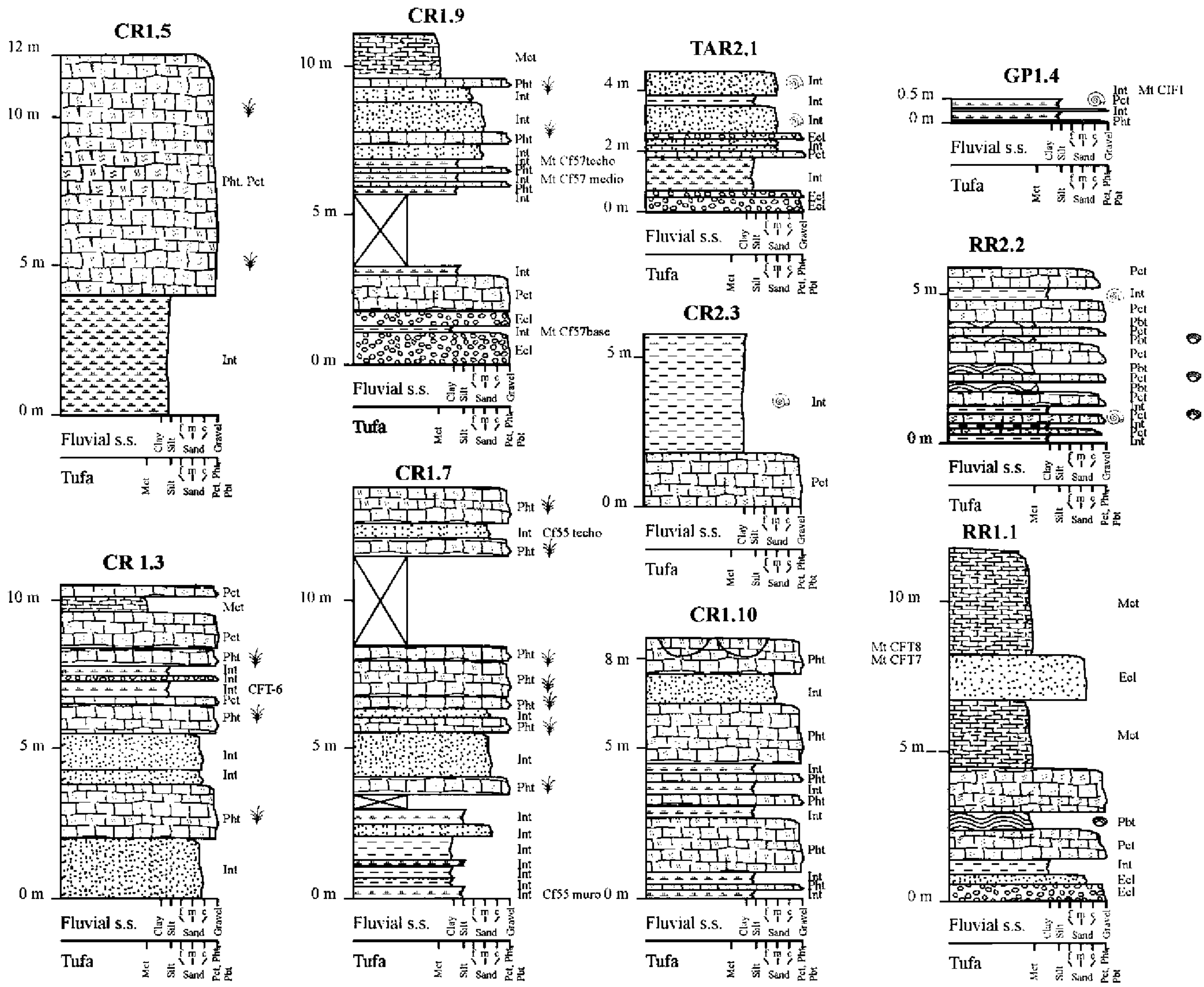

Fig. 6. Several representative stratigraphic sections of the Cifuentes, Ruguilla and Tagus rivers with the facies identified. Legend in Fig. 5.

although we selected only *Herpetocypris reptans* (Baird) individuals for the analysis.

In two localities (HR3.2 and HR4.2) gastropods were also recovered and analysed. In this case, gastropod shells were also cleaned sonicated and with water to remove sediment. Peripheral parts, approximately 20–30%, were removed after chemical cleaning of the sample with 2 N HCl. Afterwards, *ca.* 5–10 mg were selected for amino acid racemization analysis.

Analytical samples of each bed contained only single monospecific *H. reptans* valves. Amino acid concentrations and ratios were quantified using HPLC following the sample preparation protocol described by Kaufman and Manley (1998) and Kaufman (2000). This procedure involves hydrolysis, which was performed under N_2 atmosphere in 7 μL of 6 M HCl (10 μL/mg in case of gastropod samples) for 20 h at 100 °C. The hydrolysates were evaporated to dryness in *vacuo*, and then rehydrated in 7 μL 0.01 M HCl with 1.5 mM sodium azide and 0.03 mM L-*homo*-arginine (internal standard).

Samples were injected in an Agilent-1100 HPLC, equipped with a fluorescence detector. Excitation and emission wavelengths were programmed at 335 nm and 445, respectively. A Hypersil BDS C18 reverse-phase column (5 μm; 250 × 4 mm i.d.) was used for the analysis.

The derivatization took place before injection by mixing the sample (2 μL) with the pre-column derivatization reagent (2.2 μL), which comprised 260 mM isobutyryl-L-cysteine (chiral thiol) and 170 mM o-phthaldialdehyde, dissolved in 1.0 M potassium borate buffer solution at pH 10.4. Eluent A consisted of 23 mM sodium acetate with 1.5 mM sodium azide and 1.3 micro M EDTA, adjusted to pH 6.00 with 10 M sodium hydroxide and 10% acetic acid. Eluent B was HPLC-grade methanol and eluent C consisted of HPLC-grade acetonitrile. A linear gradient was performed at 1.0 mL/min and 25 °C, from 95% eluent A and 5% eluent B upon injection to 76.6 eluent A, 23% eluent B, and 0.4% eluent C at min 31.

3.2. *Stable isotope analysis*

A total of 38 samples were taken from the tufa terraces in central Spain (Cifuentes areas, Henares and Dulce rivers) for stable isotope analysis. For this purpose, a wide data set from the nearby Priego area was also used (36 samples; *cf.* Torres et al., 1995). In some cases, several samples were recovered along the stratigraphic sections. Five water samples from some of these rivers and springs were also collected for comparison with modern-day stable isotope values.

Tufa samples were dried at 50 °C and, after a mechanical removal of superficial parts, were ground to a fine powder. Carbon dioxide was evolved from the calcite using 100% phosphoric acid for 5 h in a thermostatic bath at 50 °C (McCrea, 1950; Swart et al., 1991). A Pyrex microline was used for gas purification. The carbon and oxygen stable isotope analyses were conducted in a Finnigan MAT 251 mass spectrometer at the *Estación Experimental del Zaidín* (CSIC, Granada). The isotope results are reported in the standard delta (δ) notation in parts per thousand (‰) relative to the international V-PDB standard (Gonfiantini, 1981). All the samples were compared to a reference carbon dioxide obtained from a calcite standard (internal and international standard) prepared at the same time. The experimental error for calcite ($\delta^{13}C$ and $\delta^{18}O$) was less than ±0.1%. Carrara and EEZ-1, previously compared with the international standards NBS-18 and NBS-19, were used as internal standards.

At the time of water samples collection for $\delta^{13}C_{DIC}$ analysis, they were filtered (0.45 μm) in situ by syringe into 12-ml vials followed by poisoning with $HgCl_2$ in order to avoid secondary biological activity. They were then capped leaving no headspace and stored at 4 °C. In the laboratory, samples were prepared in order to liberate CO_2 as follows: an aliquot of sample was injected into 12-ml vials pre-filled with helium and 5 drops of 65% phosphoric acid and shaken in a Vortex agitator for 30 s. The vials were then left at room temperature for between 15 and 36 h to obtain a state of equilibrium (Salata et al., 2000). The CO_2 was separated from other residual gases by chromatography using a helium carrier gas in a Gas Bench (ThermoFinnigan, Bremen, Germany) system interfaced with a mass spectrometer.

4. Results and discussion

4.1. Amino acid racemization

The *D*/*L* ratios of aspartic acid and glutamic acid measured in 233 analytical samples (Table 2) showed strong correlation coefficients ($r = 0.87$; p-level < 0.000) and were, therefore, directly related to the age of the horizons sampled (Goodfriend, 1991). We selected these amino acids because they have high racemization rates, which make them suitable to date relatively young samples. In fact, the peaks of the D enantiomers of leucine, phenylalanine and isoleucine were very small, sometimes almost negligible.

Unfortunately, ostracod valves from locality HR4.2 were contaminated, i.e., L-serine was more abundant than L-glutamic acid and L-aspartic acid (*cf.* Hearty et al., 2004), and were consequently omitted from this study. However, this locality was dated through its gastropod content (Table 3).

4.1.1. Aminostratigraphy

Aminostratigraphy consists of the relative dating of geological–paleontological localities on the basis the amino acid racemization ratios from palaeobiological samples (same genera) preserved in similar taphonomical conditions such as thermal history and geochemical parameters. Localities for which ratios are similar can be clustered in groups called aminozones, representing, in this case, an almost-isochronous event.

The use of samples from the Cifuentes–Ruguilla tufa system, the Tagus and the Henares and Dulce is justified by the fact that a similar thermal history can be inferred for these areas, as they belong to the same climatic region. The results were compared with those obtained in the Priego area-Guadiela, Escabas and Trabaque rivers (see location in Fig. 1), where a tufa system deposited during the Pleistocene is observed, and where distinct aminozones were established through the amino acid racemization ratios obtained in *H. reptans* ostracods (Torres et al., 2005).

Table 2
Mean values and standard deviation of *D*/*L* ratios of aspartic acid and glutamic acid obtained in *Herpetocypris reptans* ostracodes from the Henares, Dulce, Cifuentes, Ruguilla and Tagus rivers and Gárgoles de Arriba pond and age calculation of each level.

Locality	*D*/*L* Asp	*D*/*L* Glu	Age (ka B.P.)	*n*
HR1.1	0.421 ± 0.023	0.185 ± 0.039	198 ± 36	10
HR2.1	0.435 ± 0.016	0.182 ± 0.028	205 ± 26	4
HR2.2	0.455 ± 0.048	0.264 ± 0.049	283 ± 66	11
HR3.1	0.379 ± 0.059	0.165 ± 0.082	158 ± 10	4
HR4.1	0.366 ± 0.039	0.132 ± 0.023	132 ± 22	3
HR5.1	0.160 ± 0.041	0.049 ± 0.014	12 ± 3	5
DR1.1	0.538 ± 0.060	0.362 ± 0.066	405 ± 95	7
DR2.1	0.405 ± 0.055	0.193 ± 0.055	185 ± 42	10
DR3.1	0.376 ± 0.020	0.122 ± 0.032	138 ± 32	3
DR4.1	0.164 ± 0.010	0.043 ± 0.004	6 ± 1	4
DR4.2	0.162 ± 0.026	0.058 ± 0.037	7 ± 2	4
MH.1.1	0.419 ± 0.025	0.244 ± 0.025	239 ± 46	11
RR1.1	0.465 ± 0.058	0.313 ± 0.071	301 ± 61	6
RR2.1	0.416 ± 0.014	0.181 ± 0.016	190 ± 18	6
RR2.2	0.350 ± 0.086	0.131 ± 0.054	121 ± 55	4
CR1.1	0.333 ± 0.012	0.092 ± 0.031	97 ± 19	8
CR1.2	0.360 ± 0.015	0.120 ± 0.014	126 ± 17	7
CR1.3	0.351 ± 0.017	0.126 ± 0.018	113 ± 20	10
CR1.4	0.381 ± 0.010	0.120 ± 0.004	137 ± 16	3
CR1.5	0.374 ± 0.029	0.112 ± 0.011	127 ± 36	8
CR1.6	0.339 ± 0.031	0.114 ± 0.014	105 ± 22	4
CR1.7 bottom	0.386 ± 0.072	0.133 ± 0.043	156 ± 31	6
CR1.7 top	0.348 ± 0.017	0.135 ± 0.008	127 ± 17	6
CR1.8	0.398 ± 0.012	0.147 ± 0.006	157 ± 19	6
CR1.9 bottom	0.386 ± 0.001	0.127 ± 0.006	148 ± 12	2
CR1.9 top	0.420 ± 0.035	0.156 ± 0.032	179 ± 47	10
CR1.10	0.340 ± 0.011	0.117 ± 0.012	111 ± 19	6
CR1.11	0.341 ± 0.012	0.108 ± 0.021	102 ± 33	5
CR2.1	0.123 ± 0.005	0.031 ± 0.006	1.5 ± 0.5	2
CR2.2	0.140 ± 0.012	0.040 ± 0.007	3.5 ± 1	3
CR2.3	0.167 ± 0.005	0.043 ± 0.006	7 ± 1	4
GP1.1	0.204 ± 0.005	0.056 ± 0.006	16 ± 5	6
GP1.2	0.184 ± 0.034	0.044 ± 0.013	11 ± 4	5
GP1.3	0.199 ± 0.017	0.050 ± 0.002	13 ± 2	5
GP1.4	0.160 ± 0.009	0.041 ± 0.004	5 ± 1	5
TAR1.1	0.409 ± 0.006	0.135 ± 0.019	174 ± 20	7
TAR2.1	0.232 ± 0.014	0.061 ± 0.008	25 ± 8	7
TAR2.2	0.144 ± 0.007	0.059 ± 0.008	9 ± 2	5
TAR2.3	0.267 ± 0.018	0.063 ± 0.010	36 ± 10	7

Asp: aspartic acid; Glu: glutamic acid; *n*: number of samples.

Although the data from the Priego tufa system were obtained using a gas chromatograph, they can be compared with the aspartic acid and glutamic *D*/*L* ratios calculated in this study because of the similarities found between the racemization ratios of the samples from Wehmiller's (1984) Inter-Laboratory Comparison (ILC) exercise and several ostracod samples analysed by GC and HPLC in our laboratory (Table 4).

Eight groups (aminozones) were established with the aid of a cluster analysis (complete linkage and Euclidean distance) from the aspartic acid and glutamic acid *D*/*L* ratios obtained in samples containing *H. reptans* valves (Fig. 7). These groups were named following the nomenclature used in Torres et al. (2005), Aminozone 1 corresponding to the oldest tufa deposits and Aminozone 8 the youngest localities. The mean *D*/*L* ratios of each aminozone and the sections included in each are shown in Table 5. The eight

Table 3
Mean values and standard deviation of *D*/*L* ratios of aspartic acid and glutamic acid obtained in gastropods from the Henares river localities HR3.2 and HR4.2 and age calculation.

Locality	*D*/*L* Asp	*D*/*L* Glu	Age (ka B.P.)	*n*
HR3.2	0.461 ± 0.000	0.214 ± 0.000	89 ± 11	1
HR4.2	0.402 ± 0.067	0.159 ± 0.028	38 ± 6	2

Table 4
Comparison between the aspartic acid and glutamic acid racemization ratios of the Wehmiller's (1984) Inter-Laboratory Comparison (ILC) exercise samples and different ostracode samples analysed by GC and HPLC in our laboratory (Biomolecular Stratigraphy Laboratory). A 20-h time hydrolysis at 100 °C in hydrochloric acid under a nitrogen atmosphere was performed for all kind of samples (for the GC and the HPLC analysis). Samples CTB-182, CSU-6, CBS-352, CBS-253 and FA4 were constituted by *Cyprideis torosa* valves; samples TR4.4., TR4.3, TR4.1, ES4.1, ES6.2, RB12, RB4, RB5, RB13, CR1.1, GP1.1, SPD-3160 and SPD-0198 were constituted by *Herpetocypris reptans* individuals. For reference: The amino acid racemization ratios obtained by Wehmiller (1984) in the ILC standards analysed in a GC (hydrolysis performed during 22 h at 110 °C) were: for the ILC-A standard (*D*/*L* Asp: 0.378 ± 0.028; *D*/*L* Glu: 0.203 ± 0.011), for the ILC-B standard (*D*/*L* Asp: 0.705 ± 0.028; 0.432 ± 0.017), and for the ILC-C standard (*D*/*L* Asp: 0.894 ± 0.079; 0.849 ± 0.035). Samples TR4.4, TR4.3, TR4.1, ES4.1 and ES6.2 appear in Torres et al. (2005); samples CBS-352, CBS-253, FA, SPD-0198, and SPD-3160 appear in Ortiz et al. (2004); samples CTB-182, CSU-6, RB12, RB4, RB5, RB13, CR1.1 and GP1.1 were not previously published.

Sample	*D*/*L* Asp (GC)	*D*/*L* Asp (HPLC)	*D*/*L* Glu (GC)	*D*/*L* Glu (HPLC)
ILC-A	0.377 ± 0.019	0.373 ± 0.002	0.194 ± 0.009	0.204 ± 0.004
ILC-B	0.724 ± 0.007	0.673 ± 0.007	0.407 ± 0.017	0.380 ± 0.004
ILC-C	0.894 ± 0.010	0.839 ± 0.003	0.804 ± 0.009	0.818 ± 0.008
CTB-182	0.742 ± 0.035	0.701 ± 0.021	0.704 ± 0.083	0.595 ± 0.028
CBS-253	0.700 ± 0.013	0.682 ± 0.037	0.534 ± 0.042	0.532 ± 0.070
CSU-6	0.584 ± 0.007	0.561 ± 0.022	0.373 ± 0.009	0. 380 ± 0.049
FA	0.587 ± 0.000	0.557 ± 0.030	0.364 ± 0.000	0.408 ± 0.034
TR4.4	0.482 ± 0.001	0.475 ± 0.035	0.228 ± 0.001	0.227 ± 0.004
CBS-352	0.441 ± 0.019	0.420 ± 0.024	0.325 ± 0.005	0.308 ± 0.048
RB4	0.437 ± 0.035	0.455 ± 0.020	0.261 ± 0.056	0.277 ± 0.037
SPD-3160	0.401 ± 0.010	0.385 ± 0.020	0.140 ± 0.005	0.153 ± 0.005
TR4.3	0.375 ± 0.001	0.377 ± 0.016	0.122 ± 0.008	0.140 ± 0.006
CR1.1	0.335 ± 0.001	0.333 ± 0.012	0.116 ± 0.005	0.107 ± 0.012
TR4.1	0.333 ± 0.002	0.317 ± 0.016	0.117 ± 0.001	0.122 ± 0.013
ES4.1	0.327 ± 0.001	0.339 ± 0.012	0.111 ± 0.002	0.111 ± 0.013
RB12	0.279 ± 0.000	0.306 ± 0.012	0.080 ± 0.000	0.087 ± 0.002
RB5	0.287 ± 0.005	0.283 ± 0.024	0.088 ± 0.003	0.079 ± 0.015
RB13	0.201 ± 0.020	0.189 ± 0.010	0.052 ± 0.010	0.043 ± 0.002
GP1.2	0.190 ± 0.001	0.184 ± 0.034	0.049 ± 0.001	0.050 ± 0.005
ES6.2	0.184 ± 0.002	0.218 ± 0.014	0.048 ± 0.001	0.057 ± 0.002
SPD-0198	0.182 ± 0.000	0.183 ± 0.003	0.056 ± 0.001	0.049 ± 0.008

aminozones were further used for group identification (Fig. 8A and B), being noteworthy that *D*/*L* Asp values allowed better differentiation between intermediate age sections.

Two new Aminozones (6 and 7), additional to those observed in the Priego area, were distinguished. Aminozone 6 includes two localities sampled along the Tagus river, while the lowest terraces of the Cifuentes, Dulce and Tagus rivers coincide with Aminozone 8.

In general, good correspondence was observed between the fluvial terrace levels of the Henares, Dulce, Tagus and Ruguilla rivers, on the basis both of relative elevation above their current river thalweg, and the aminozones. In general, the highest terrace levels are the oldest tufa deposits, whereas the lowest localities are the youngest. However, a number of exceptions were observed. The highest deposits of the Henares river (HR1.1), which are +50 to 60 m above the current river thalweg, were grouped with other localities (HR2.1 and HR3.1-Aminozone 3) located much lower (+30 to 40 m, +15 to 25 m, respectively). Moreover, HR2.2, which is +30 m above the current Henares river thalweg, was included within an older Aminozone (2). In our opinion, this observation can be explained by episodes of re-deposition and re-excavation of a pre-existent valley.

Locality MH1.1, which is linked to a small tributary creek and could not be grouped on the basis of its elevation, was included in Aminozone 2. Samples recovered from the Gárgoles de Arriba lacustrine deposits (GP1.1 to GP.1.4) were all included within the episodes of the youngest tufa terraces (mainly Aminozones 7 and 8).

However, an apparent poor correspondence was found between the fluvial terrace levels of the Cifuentes river. All the highest terrace levels of this river (10–20 m above the current river thalweg) were indistinctively included in Aminozones 4 and 5, except CR1.8 and CR1.9 top, which belonged to Aminozone 3. This finding can be explained by the construction of paludal tufas which infilled a pre-existing palleovalley. In fact, according to Pedley et al. (2003), these deposits are organized into a series of prograding thin lobes down the paleovalley that are superimposed on each another. These lobes also extend in a transverse section towards the valley axis.

All the samples from the lowest tufa deposits of the Cifuentes river (CR2.1-CR2.3) were grouped in Aminozone 8.

4.1.2. Aminochronology

The numerical age of each terrace was calculated using the aspartic acid and glutamic acid *D*/*L* ratios. For ostracods *H. reptans*, the age calculation algorithms applied were those established by

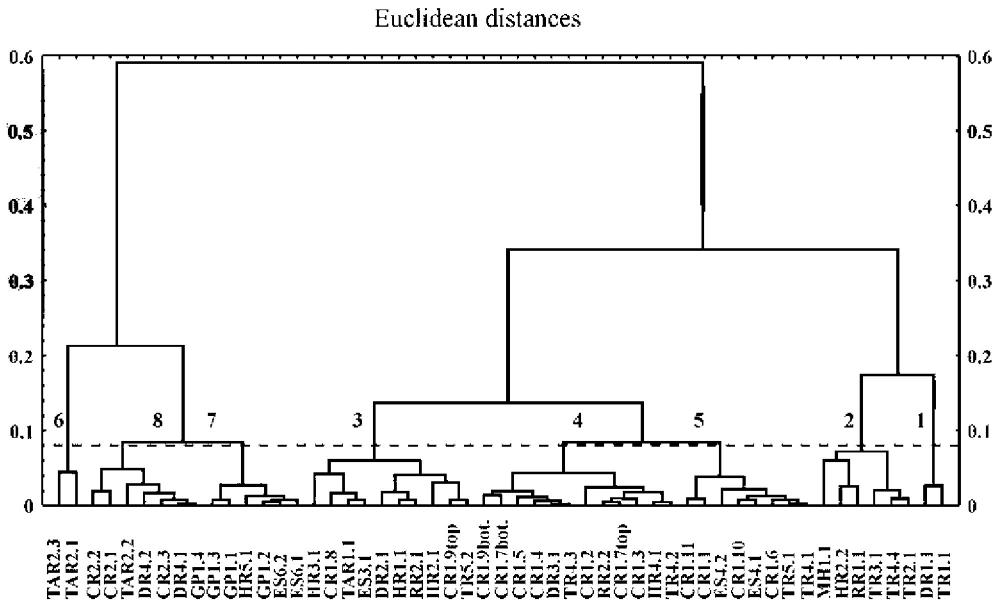

Fig. 7. Dendogram (complete linkage and Euclidean distance) of the *D*/*L* Asp and *D*/*L* Glu values of ostracods from tufa deposits in the Henares, Dulce, Cifuentes, Ruguilla and Tagus rivers, the Gárgoles lake and the Priego area. Each cluster was identified to an Aminozone (A1 – oldest to A8 – youngest).

Table 5
Mean values and standard deviation of aspartic acid and glutamic acid *D/L* ratios that characterize the ostracode aminozones established in central Spain tufa deposits (Tagus, Henares, Dulce, Ruguilla and Cifuentes rivers, Gárgoles de Arriba pond and Priego area). The average age of the different Aminozones is also presented.

Aminozone	Localities	*D/L* Asp	*D/L* Glu	Age (ka B.P.)
1	TR1.1, DR1.1	0.541 ± 0.052	0.360 ± 0.060	406 ± 90 (MIS 11)
2	TR2.1, TR3.1, TR4.4, RR1.1, HR2.2, MH1.1	0.452 ± 0.042	0.264 ± 0.050	264 ± 68 (MIS 7e)
3	ES3.1, TR5.2, HR3.1, CR1.8, TAR1.1, DR2.1, HR1.1, RR2.1, HR2.1, CR1.9-top	0.412 ± 0.031	0.166 ± 0.038	189 ± 40 (MIS 7a)
4	TR4.2, TR4.3, CR1.9 bottom, CR1.7 bottom, CR1.5, CR1.4, DR3.1, CR1.2, RR2.2, CR1.7 top, CR1.3, HR4.1	0.366 ± 0.037	0.126 ± 0.021	130 ± 27 (MIS 6/5)
5	TR2.1, TR5.2, ES4.1, ES4.2, CR1.1, CR1.10, CR1.11, CR1.6, HR3.2[a]	0.335 ± 0.016	0.110 ± 0.015	101 ± 25 (MIS 5c)
6	TAR2.1, TAR2.3, HR4.2[a]	0.250 ± 0.024	0.062 ± 0.009	32 ± 10 (MIS 3)
7	ES6.1, ES6.2, GP1.1, GP1.2, GP1.3, HR5.1	0.195 ± 0.015	0.052 ± 0.005	14 ± 4 (MIS 1)
8	CR2.1, CR2.2, TAR2.2, DR4.1, DR4.2, CR2.3, GP1.4	0.154 ± 0.017	0.044 ± 0.009	6 ± 2 (MIS 1)

[a] Gastropod samples dated with the amino acid racemization method are included in the mean age of the Aminozones.

Ortiz et al. (2004) in the central and southern part of the Iberian Peninsula. For the age calculation of the gastropod samples (HR3.2 and HR4.2), we used the algorithms established by Torres et al. (1997) for freshwater gastropods (*Radix* and *Planorbis* genera) of the central and southern part of the Iberian Peninsula.

Numerical dating was done by introducing the *D/L* ratios into the algorithms of each amino acid. The age of a single terrace section is the average of the numerical dates obtained for each amino acid *D/L* ratio measured in gastropods from that locality (Table 3). The age uncertainty of a section is the standard deviation of all the values obtained.

The amino acid racemization method provided an age of 405 ± 95 ka for DR1.1, which is consistent with the results of two samples from this section, which were previously dated by U/Th at >350 ka (Ordóñez et al., 1990).

According to Ordóñez et al. (1987), the tufa deposits located south of Gárgoles de Abajo (+15 to 20 m), on the right side of the Cifuentes river (CR1.11), formed during two phases. At this point, the carbonate constructions presented fissures, filled by lutites, which developed after extensive erosion and partial dismantling of the previous tufa deposits (*cf.* Pedley et al., 2003). One of the samples dated in this area was collected at the tufa horizon (CR1.11) and another was taken in one of these nested depressions (CR1.10) which consisted of beige and brown marls with phytoclasts (mainly grass and *Typha* coated stems) and abundant gastropod shells (*Radix*) linked to paludal facies. The age of these fissure-fill deposits (102 ± 33 ka) reflects that the karst process began immediately before the tufa horizon build up, which was dated at 111 ± 19 ka.

Our datings differ from those obtained by Ordóñez et al. (1990) in Ruguilla and Cifuentes tufa deposits using the U/Th method. In our opinion, those data reflect either open-system conditions or detrital contamination and, therefore, are doubtful. The sample M-3 of Ordóñez et al. (1990), which corresponds to "a terrace near Ruguilla (+40 m above the Ruguilla river – 301 ± 61 ka)", and equivalent to our sample RR1.1, was dated at >350 ka, and sample M-4 "(Sotoca, +10 m above the Ruguilla river)", equivalent to our samples RR2.1 (190 ± 18 ka) or RR2.2 (121 ± 55 ka), was dated at 226.9 (+68.7, −44.0) ka. In our opinion these ages are greater than the true ones because the $^{230}Th/^{234}U$ ratio in these samples is higher or almost 1 (*cf.* Ordóñez et al., 1990), which according to Horvatinčić et al. (2000) can be attributed to uranium leaching and, therefore, should not be taken into account.

Sample M-5 of Ordóñez et al. (1990) (Gárgoles de Abajo, +15 to 18 m above the Cifuentes river), equivalent to our sample CR1.6 (105 ± 22 ka), was dated at 91.9 (+69.2, −50.6) ka and samples M-6 and M-7, collected in some fluvial dams of the Tagus river, south of Trillo, gave, respectively, 40.7 (+46.9, −30.4) ka and 54.9 (+11.2, −10.1) ka, similar to those obtained in our study (*cf.* TAR2.1 and TAR2.3). However, these samples were probably contaminated (*cf.* Ordóñez et al., 1990) with post-depositional carbonates because the ratios $^{230}Th/^{232}Th$ were lower than 20 in all cases, which indicates considerable inputs of detrital thorium (Schwarcz, 1980; Ford and Schwarcz, 1981; Bischoff et al., 1994; Horvatinčić et al., 2000; Auler and Smart, 2001). In fact, the standard error of samples M-5 and M-6 was very high, but they provided similar results to those presented in this paper and obtained by amino acid racemization dating.

Using the U/Th method, Howell et al. (1995) dated the uppermost tufa terrace of Horna (+30 m) at 440 ± 70 ka. These authors also dated the deposits located 22 m above current river thalweg in the vicinity of Alcuneza (equivalent to our sample HR2.2: 283 ± 66 ka) at 243 ± 18 ka and 202 ± 58 ka, and the terrace level placed 15 m above the Henares river (equivalent to our samples HR3.1: 158 ± 10 ka; HR4.1: 132 ± 22) at 135 ± 12 ka and 103 ± 8 ka. Therefore, the dates reported by Howell et al. (1995) coincide with our results.

However, the age of section HR5.1 (12 ± 3 ka) was slightly older than that reported by Gladfelter (1971, 1972) – 6560 ± 130 yr B.P. (^{14}C) – and Preece (1991) – 9940 ± 120 yr B.P. (^{14}C) and 5160 ± 90 yr B.P. (^{14}C) – for the bottom and top of this section, respectively.

The average age of each aminozone was also calculated using the individual ages of the sections included in it (Table 5).

On the basis of all previous studies of the tributaries of the Tagus and the observation of the current study, we distinguished eight tufa-deposition episodes in the central part of the Iberian Peninsula (Fig. 8, Table 5). Six of these (Aminozones 1, 2, 3, 4, 5 and 8) were observed in the Priego area, located southeast of the Cifuentes zone, where three Tagus tributaries (the Trabaque, Escabas and Guadiela rivers) have produced tufa terraces, which were studied and dated by the amino acid racemization method (*cf.* Torres et al., 2005).

Six tufa-deposition episodes (Aminozones 2, 3, 4, 5, 7 and 8) recorded in the Cifuentes–Ruguilla area were correlated with distinct interglacial episodes. The second episode was represented in this area by the highest tufa deposits that occur on the flat-top of several mesas around Ruguilla, +40 to 50 m above the current river thalweg. This tufa terrace was correlated with the MIS 7e.

Of note, the seventh tufa formation episode, dated at 14 ± 4 ka, was found in this area only in the Gárgoles de Arriba lake. In our opinion, the increase in precipitation associated with climatic amelioration, which occurred at the end of the Last Glacial Maximum, and the existence of highly cemented sandstone beds of Miocene age which acted as a dam, forming a local-base level (in fact, today there is a waterfall in the vicinity of Gárgoles de Arriba produced by these horizons), produced extensive ponding and expansion of the lake.

Five tufa terraces were observed along the Henares valley (Aminozones 2, 3, 4, 6 and 7), four tufa terraces occurred linked to the Dulce river (Aminozones 1, 3, 4 and 8), and three tufa-deposition episodes were found along the Tagus (Aminozones 3, 6 and 8).

The average ages of the different Aminozones (Table 5) indicate that almost all the episodes of tufa deposition fell within odd Marine Isotope Stages (11, 7e, 7a, 5c, 3 and 1) except the fourth one, which can be placed in a period from the end of MIS 6 to the

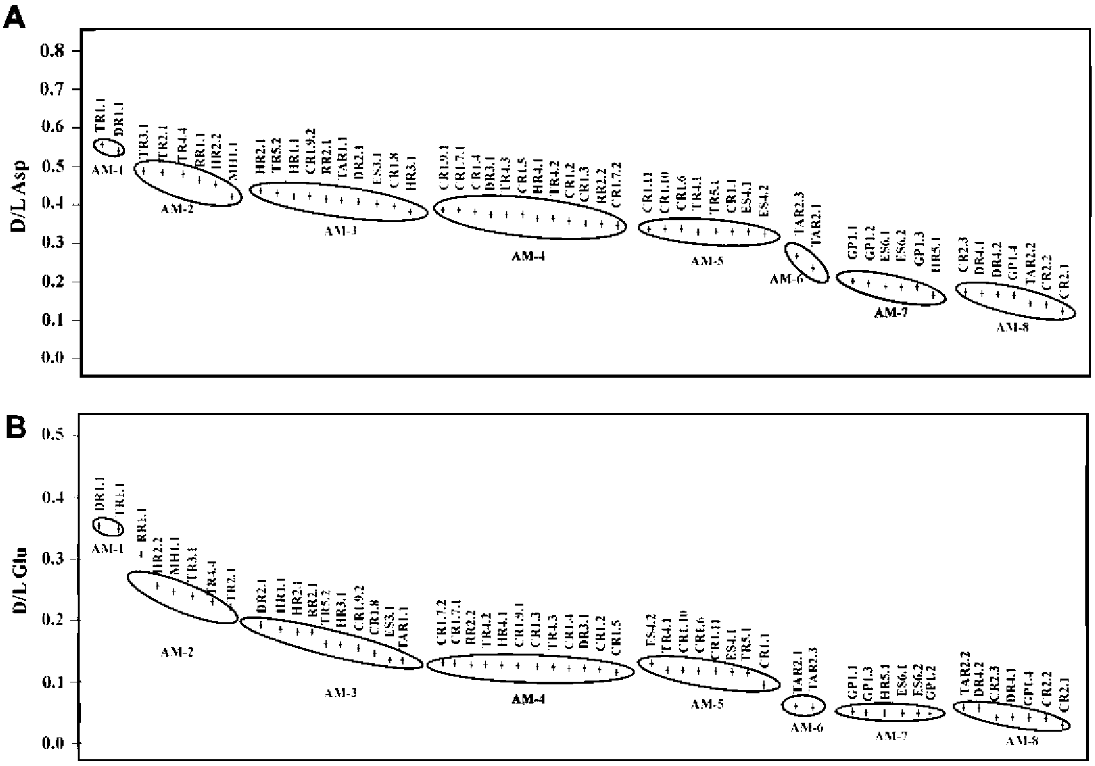

Fig. 8. Aminostratigraphy of the stratigraphic sections of tufa deposits in central Spain (the Henares, Dulce, Cifuentes, Ruguilla, and Tagus rivers and the Gárgoles lake – this paper; the Trabaque, Guadiela and Escabas rivers (Priego area) – Torres et al., 2005) based on the mean *D*/*L* Asp (A) and *D*/*L* Glu (B) values obtained from ostracod valves.

beginning of MIS 5e. Two of the episodes occurred in the MIS 1, the first at the end of the Last Glacial Maximum, and the second in the Middle Holocene.

4.2. Stable isotope analysis

The stable isotopes (δ^{18}O, δ^{13}C) in tufa deposits are related to the environmental conditions, such as temperature and water δ^{18}O values, and vegetation cover. Nevertheless, some carbon within the DIC (Dissolved Inorganic Carbon) category can be derived from other sources, like the dissolution of bedrock in the catchment area, requiring caution in interpretation.

The stable isotope data of Pleistocene and Holocene tufa deposits from the Tagus Basin (Cifuentes area, Henares and Dulce rivers), including those of the Priego area (Fig. 1), are plotted in Fig. 9. δ^{18}O values ranged from −5.42‰ to −7.93‰ (V-PDB) while δ^{13}C values oscillated between −4.5‰ to −10.77‰ (V-PDB). Samples of the same age and stratigraphic sections, that is, with similar environmental conditions, and even with distinct morphologies and textures, showed similar δ^{18}O and δ^{13}C values (Fig. 9). Consequently, in Fig. 9 different types of freshwater and microbial precipitates (dense and porous crusts, moss and twig tufa, oncoids) from each area are plotted together.

Similar ranges of δ^{18}O values were obtained in all the areas sampled. However, less correspondence was observed in the δ^{13}C values: in the Priego area, most of these values fell in a narrow field, between −6‰ and −7‰ (V-PDB), while tufa deposits of the Henares and Dulce rivers showed the lowest δ^{13}C values (>8‰ vs V-PDB). In the Cifuentes area, the δ^{13}C oscillated between −5.6‰ and −8.7‰ (V-PDB), although it was typically between −6.5‰ and −7.5‰ and in terraces of the Ruguilla river δ^{13}C values varied between −6.5 and −9.0‰ (V-PDB). Similar oxygen and carbon stable isotope values as those registered in Priego and Cifuentes were detected in the nearby area of Puente San Pedro (Guadalajara) (López Vera and Martínez Goytre, 1988, 1989). In contrast, Ordóñez et al. (1981) reported similar δ^{13}C and δ^{18}O values in the Tajuña and Dulce rivers to those we found in the Henares, Dulce and Ruguilla rivers. Likewise, the δ^{13}C and δ^{18}O values obtained in our study fell within the typical oxygen and carbon stable isotope ratios of modern European microbial carbonates of "lowland streams and wooded Alpine streams" or of "British Isles rivers" (Andrews et al., 1994, 1997).

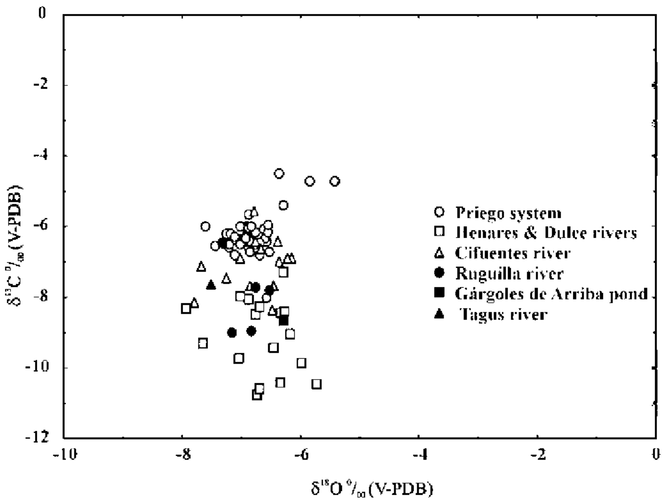

Fig. 9. Stable oxygen and carbon isotope data for the six areas distinguished in this paper (the Priego area, the Henares, Dulce, Cifuentes, and Ruguilla rivers, Gárgoles lake and the Tagus river).

4.2.1. *Oxygen isotopes*

In carbonate tufa-deposition settings the $\delta^{18}O$ of the resultant tufa is driven mainly by $\delta^{18}O$ values of water, temperature and equilibrium conditions (Epstein et al., 1953; O'Neil et al., 1969; Kim and O'Neil, 1997). It has been shown (Pentecost and Spiro, 1990; Pentecost, 1992; Andrews et al., 1993, 1997) that present day tufas have $\delta^{18}O$ values that are closely related to the $\delta^{18}O$ in the regional precipitation and that the values are moderated by other factors, such as water temperature changes, evaporation and residence time. In fact, our tufa $\delta^{18}O$ and $\delta^{13}C$ values were relatively alienated around the local MCL (Meteoric Carbonate Line), as described by Lohmann (1987) for continental carbonates (Fig. 9).

In the present study, most of the $\delta^{18}O$ values in tufa deposits comprised between -6 and $-8‰$ (V-PDB). This range allowed the calculation of the oxygen isotopic range of the water in which the tufa was precipitated (see Fig. 10). For this purpose we considered the extreme temperature conditions of tufa precipitation (5–25 °C), although the current mean annual temperature of these areas is around 15 °C (Rivas-Martínez and Rivas y Sâenz, 2008). The theoretical $\delta^{18}O_{water}$ values (V-SMOW) calculated ranged between -10.1 and $-4‰$, which are in agreement with oxygen isotope values of the present local meteoric waters analysed (-9 to -7.7 vs V-SMOW) (Araguás Araguás and Díaz-Teijeiro, 2005) and of lakes within the Tagus basin (Valero-Garcés et al., 2008).

Thus, the theoretical $\delta^{18}O$ values of tufas in equilibrium with the present conditions (water and temperature) gave values that were consistent with the experimental measurements (Figs. 9 and 10) and present day tufas from this basin (-8 to $-6‰$ vs V-PDB, Valero-Garcés et al., 2008). Therefore, the $\delta^{18}O$ values of the study areas indicate meteoric water-origin, with values characteristic of freshwater carbonate environments (Turi, 1986; Casanova, 1986; Ordóñez et al., 2005; Andrews et al., 1993), and are similar to those found in Holocene and Pleistocene Spanish localities (Andrews et al., 2000; Arenas et al., 2000; Valero-Garcés et al., 2008), and even to those reported by Zamarreño et al. (1997) of Upper Paleocene and Eocene ages. This similarity indicates that palaeoclimatic

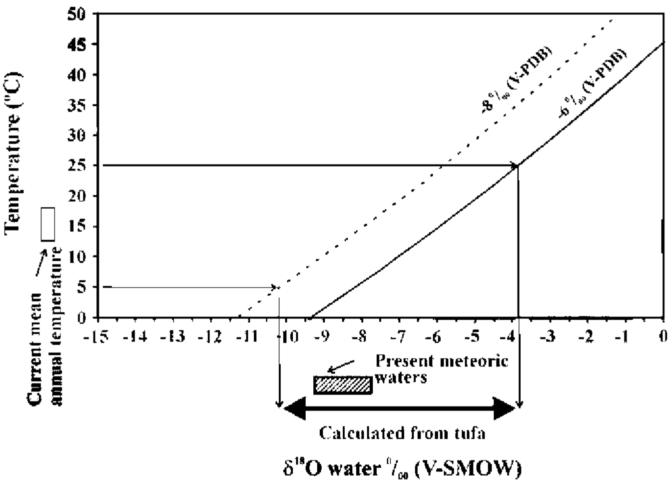

Fig. 10. Diagram showing temperature and $\delta^{18}O‰$ (V-SMOW) values of waters. The curves represent the theoretical temperature of the formation of calcite in equilibrium with river waters. Kim and O'Neil's (1997) calcite–water equation was used for calculation. The widest temperature range (5–25 °C) for tufa precipitation and the most frequent range of isotopic values measured in tufas from the Tagus Basin fluvial terraces ($-8‰<\delta^{18}O<-6‰$ vs V-PDB) were used to calculate the corresponding $\delta^{18}O‰$ (V-SMOW) composition of the waters from which they were precipitated. For comparison, present values of meteoric and Tagus river waters (Valero-Garcés et al., 2008) are plotted.

conditions that favored the formation of tufa deposits were alike in central Spain during the Pleistocene and Holocene.

However, certain differences were observed in the $\delta^{18}O$ values. The range of $\delta^{18}O$ values was quite large, especially in the Priego area (-5.42 to $-7.61‰$ vs V-PDB) and localities of the Dulce and Henares rivers (-5.72 to $-7.93‰$ vs V-PDB) compared with the Cifuentes (-6.14 to $-7.80‰$) and Ruguilla (-6.52 to $-7.32‰$) areas. These observations suggest that the values are moderated by other effects (*cf.* Andrews et al., 2000; Matsuoka et al., 2001).

The amount and isotopic composition of rainwater should also be taken into account. As temperature falls, the ^{18}O content of rainwater decreases (Dansgaard, 1964; Rozanski et al., 1993; Longinelli and Selmo, 2003), while in the calcite that forms in equilibrium with rainwater the opposite occurs. These two phenomena overlap, thereby complicating the task of establishing a simple relationship between temperature and the isotope composition of the calcite (Delgado, 1994; Delgado and Reyes, 2001). The thermo-dependence fractionation factor (α) for oxygen during calcite precipitation is 0.24‰ per degree centigrade (Craig, 1965; O'Neil et al., 1969; Kim and O'Neil, 1997). Furthermore, a 1 °C temperature decrease lowers rainwater $\delta^{18}O$ values by 0.69‰ (Dansgaard, 1964), although this value depends on latitude, averaging 0.35–0.40‰ for the Mediterranean area (Hauser et al., 1980; Delgado et al., 1991), being 0.37‰ for central Spain (Araguás Araguas and Díaz-Teijeiro, 2005). As a net result, the effect of precipitation amounts is usually greater than temperature.

In this regard, Andrews et al. (2000) report that there is a modern rainfall isotopic variability in central Iberian Peninsula produced by the Atlantic Ocean/Mediterranean Sea influence. When Mediterranean moisture, which is relatively enriched in ^{18}O, reaches this region it produces less negative $\delta^{18}O$ records, whereas when the relatively cold North Atlantic airmasses arrive, they produce heavily depleted rainfall $\delta^{18}O$ values. In fact, Leng and Marshall (2004) observed that the "precipitation amount effect" is intensified in continental settings with marked seasonal variations.

Thus, we consider that the differences in $\delta^{18}O$ values observed in central Spain tufas could be linked to rainfall rather than to temperature variations. In fact, all these tufa desposits were precipitated during odd MIS, thereby marking certain palaeoclimatic conditions with relatively higher temperatures.

4.2.2. *Carbon isotopes*

The $\delta^{13}C$ values of tufas reflect: (1) the relative contribution of isotopically light CO_2 from soil organic matter, and isotopically heavier carbon derived from the dissolution of the aquifer limestone (Andrews et al., 1993, 1997; Andrews, 2006); and (2) the equilibration of stream water with atmospheric CO_2 (degassing) (Usdowski et al., 1979; Chafetz et al., 1991). Likewise, the Rayleigh-type fractionation produces more $\delta^{13}C$ negative values in the final episodes (*cf.* Andrews and Brasier, 2005), in contrast to biological activity (photosinthesis), which preferentially consumes ^{12}C (Spiro et al., 1993).

Most of the tufas examined in central Spain showed $\delta^{13}C$ values in equilibrium with present DIC (Fig. 11). This observation implies precipitation in open systems with a carbon origin related to the decay of vegetation cover (mainly C3 plants) (Andrews et al., 1993). Nevertheless, variations in tufa $\delta^{13}C$ values were detected between the Priego area and the Cifuentes river vs the Henares, Dulce and Ruguilla rivers (the $\delta^{13}C$ values of the last three mentioned were about 3‰ more negative than the rest of localities (Figs. 10 and 11)). As the altitude, temperature in the study areas are similar, and also the catchment areas are located in the same carbonated Mesozoic formations, and with the same kind of vegetation, these variations in tufa $\delta^{13}C$ values probably record other processes. The slightly less negative $\delta^{13}C$ values observed in the Priego area and Cifuentes river

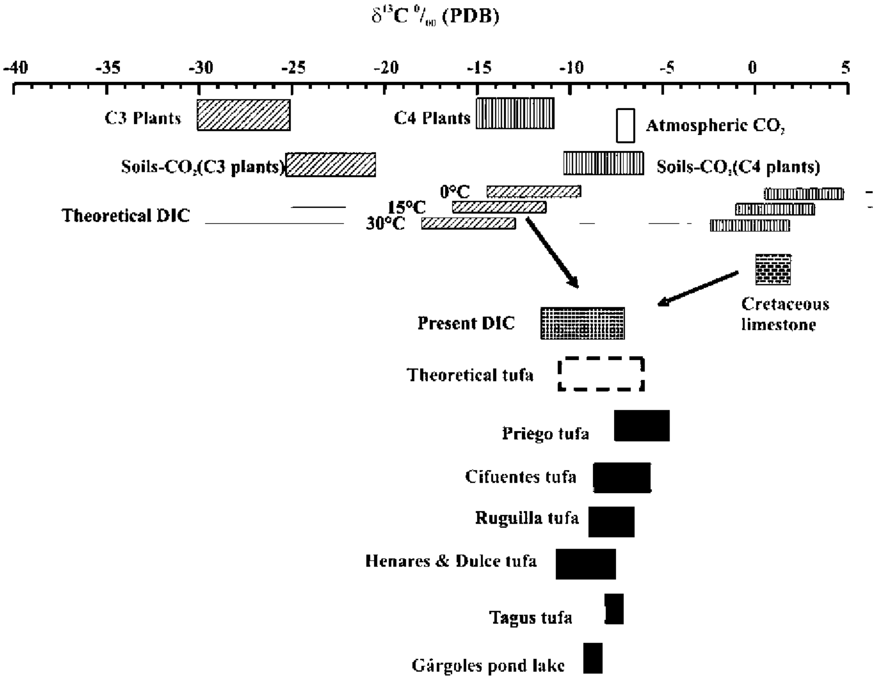

Fig. 11. Graph of the distinct sources of carbon vs tufa $\delta^{13}C$ values. Only C3 plants and atmospheric CO_2 have been considered, since CAMP and C4 plants are not present in this zone. The shaded area shows the most frequent range of C3 plants (−30‰ to −25‰) (Deines, 1980). The pre-industrial atmospheric CO_2 has a $\delta^{13}C$ value of −6.5 (Friedli et al., 1986) (−8‰ at present). The soil CO_2 is about 4.5‰ heavier than the plant biomass (Cerling, 1984; Cerling, 1991). The isotopic difference between CO_2 and dissolved inorganic carbon (DIC) depends on the pH and temperature. This value will be near 0‰ at values close to pH 5, but is relatively independent of pH between 7.5 and 8 (Romanek et al., 1992). For the isotopic theoretical calculation (DIC and tufa) we considered a calcite–bicarbonate enrichment of 1 ‰ (independent of the temperature) and the calcite–CO_2 equation described by Romanek et al. (1992) for temperatures of 0 °C, 15 °C and 30 °C. For comparison, we added the mean $\delta^{13}C$ value of cretaceous limestones from this area (Valero-Garcés et al., 2008), the $\delta^{13}C$ range of present DIC values measured in rivers of this zone, and $\delta^{13}C$ values of tufas studied in this paper separating the different tributaries.

tufas might be associated with increased input of the carbon derived from dissolution of the Mesozoic limestone outcrops. In this regard, according to Andrews et al. (1993, 1997), tufa $\delta^{13}C$ values lower than −8‰, like many of those reported in the present study, usually indicate strong soil-zone influence, whereas higher values reflect greater aquifer limestone-derived carbon input, with $\delta^{13}C$ values *ca.* +1.0‰ in this area (Valero-Garcés et al., 2008). However, the positive correlation with the $\delta^{18}O$ values (see Fig. 9) indicates that tufa precipitation in the Priego area was also probably linked to evaporation processes, which produced enrichment in ^{18}O and ^{13}C in water (Talbot, 1990; Schwalb et al., 1999; Valero-Garcés et al., 2000; Schwalb and Dean, 2002). This hypothesis is reinforced by the $\delta^{13}C$ signal of present day river waters, which is lower than −9.50‰ V-PDB (Table 6, and Valero-Garcés et al., 2008), and spring waters (−7.91‰ V-PDB in Priego area-Table 6; *ca.* −11‰ V-PDB – Valero-Garcés et al., 2008). These observations therefore indicate little influence of the catchment geochemistry.

Therefore, the influence of the types of tufa studied here (fluvial/palustrine) cannot be discarded because water flushing prevents microenvironmental effects (Andrews et al., 1997). Furthermore, the turbulence of running waters produces preferential $^{12}CO_2$ degassing (Pentecost and Spiro, 1990; Chafetz et al., 1991; Andrews et al., 1993; Andrews, 2006) and produces higher $\delta^{13}C$ signals.

Table 6
Carbon isotopic values in central Spain waters.

Sample	$\delta^{13}C$ (PDB) (DIC)
Tagus river	−9.86
Priego spring	−7.91
Tagus spring	−10.26
Guadiela river	−9.63
Trabaque river	−10.10

Likewise, photosynthesis of cyanobacteria produces environments with a DIC pool preferentially enriched in ^{13}C (Pentecost and Spiro, 1990; Andrews et al., 1997, 2000; Arp et al., 2001). However, the effects of higher plant photosynthesis on DIC $\delta^{13}C$ appear to be negligible (Usdowski et al., 1979), although they can become significant in small stagnant pools (Liu et al., 2005). In fact, in the opinion of Pavlović et al. (2002) and Horvatinčić et al. (2003), macrophytes affect Holocene tufa $\delta^{13}C$ values in Croatia.

Thus, the tufa $\delta^{13}C$ values of the Ruguilla, Henares and Dulce rivers, interpreted as having been formed by slow stream waters, indicate a major influence of soil-derived carbon. In contrast, the carbon isotope values of Priego and Cifuentes deposits indicate the existence of running waters, considerable evaporation and biological influence, mainly cyanobacteria and algae. In fact, in the Priego area (*cf.* Torres et al., 2005), the sedimentary features of the tufa systems reveal a mixture of conventional fluvial sediments (extraclastic-in-nature deposits), riverine tufa and barrage deposits (boundstone facies characterized by large stromatolites). Furthermore, the presence of large accumulations of encrusted macrophytes (mostly *Typha*) in life-position in some localities could produce stagnant pools enriched in $\delta^{13}C$ (*cf.* Pavlović et al., 2002; Horvatinčić et al., 2003; Liu et al., 2005).

The deposits of the Gárgoles de Arriba lake registered $\delta^{13}C$ values that suggest high residence times and equilibrium between atmospheric CO_2 and DIC.

4.3. Comparison with other European records

These results show good correspondence with data from other tufa deposits of central Europe (Ilm, Neckar, Tonna and Wipper rivers, Germany; Seine, Allier and Somme rivers, France; Danube river, Hungary; Krka river and Plitvice lakes, Croatia) and Spain

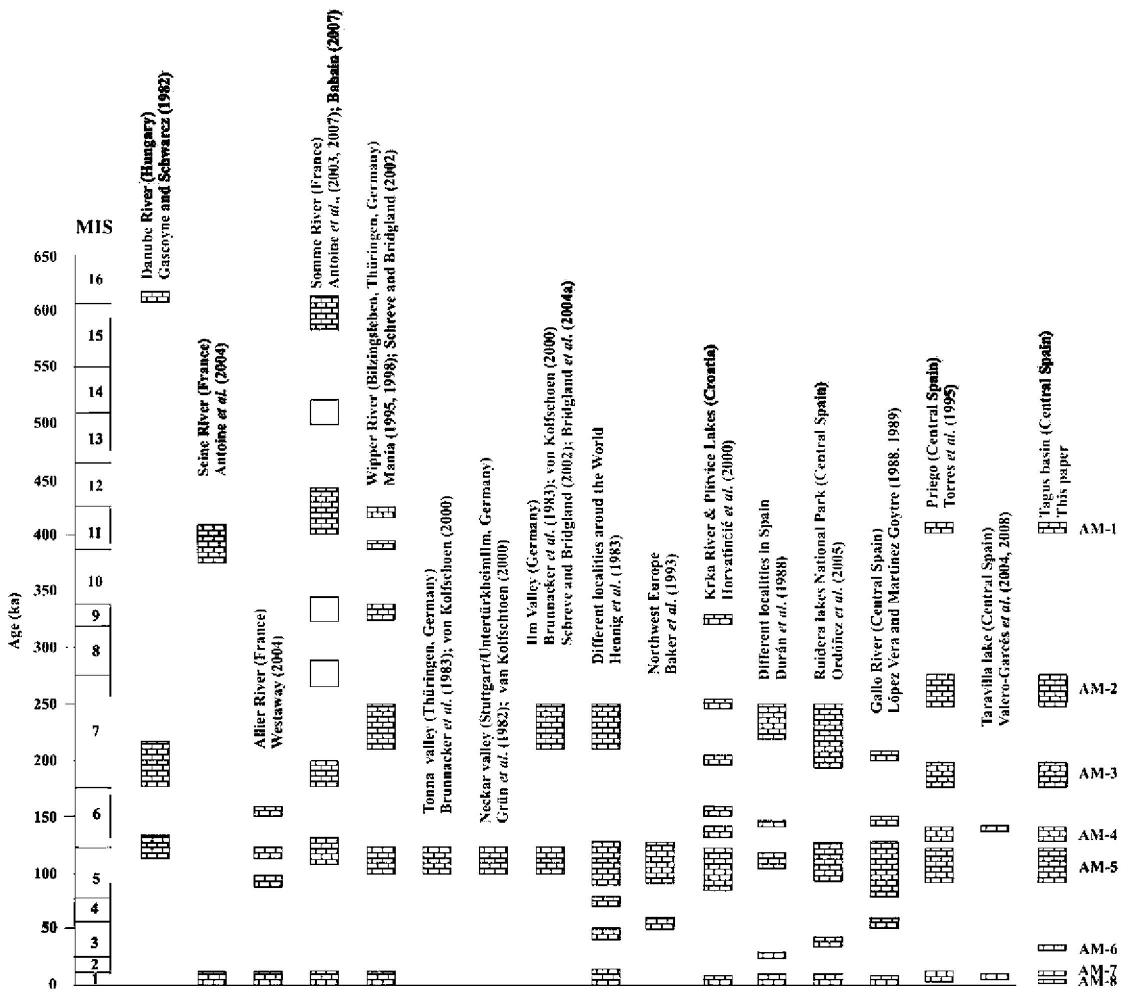

Fig. 12. Aminochronology of stratigraphic sections of the Priego area after the numerical age calculation from *D/L* Asp and *D/L* Glu values. These ages are correlated with the marine Marine Isotope Stages (MIS) and with other tufa fluvial sequences of Europe. Clastic fluvial deposits are shown in grey.

(Ruidera Lakes, Gallo river, Taravilla lake) (Fig. 12). Previous studies of speleothems and tufa in central Europe and the Mediterranean area (Geyh, 1970; Franke and Geyh, 1970; Gascoyne and Schwarcz, 1982; Grün et al., 1982; Brunnacker et al., 1983; Henning et al., 1983; Durán et al., 1988; López Vera and Martínez Goytre, 1988, 1989; Falguères et al., 1992; Baker et al., 1993; Mania, 1995, 1998; Horvatinčić et al., 2000; von Kolfschoten, 2000; Schreve and Bridgland, 2002; Antoine et al., 2003, 2007; Antoine and Limondin-Lozouet, 2004; Bridgland et al., 2004a; Westaway, 2004; Valero-Garcés et al., 2004, 2008; Ordóñez et al., 2005; Torres et al., 2005; Bahain et al., 2007) indicate that these were formed preferentially during warm interglacial and interstadial periods, that is to say during odd-numbered MIS (Fig. 12). In fact, the oxygen and carbon stable isotope values are similar to those registered in lowland European stream tufas. Likewise, Holocene tufas are found mainly in temperate, humid climates, whereas tufa growth is slowed by cold conditions. Semi-arid conditions can rarely maintain the high water tables necessary for sustained tufa deposition (Pedley, 1990). In addition, tufa deposits are found in areas where limestones are exposed in the valley slopes (Pentecost, 1995; Torres et al., 2005). Otherwise, fluvial terraces are formed by clastic (gravels and sands) materials.

Geochronological age estimates of Central European fluvial deposits are provided by various means: radiocarbon, U-series, electron spin resonance (ESR), optically stimulated luminescence (OSL) and amino acid racemization (*cf.* papers cited above). In some cases, like in the Somme and Seine rivers, tufa deposits were dated with reference to overlying well developed loess and palaeosol sequences (Antoine, 1990, 1994; Antoine et al., 2007). Likewise, some of them were also dated by their mollusk and vertebrate content. In fact, the interglacial periods frequently supported a greater diversity of animal species than the intervening glacial periods, together with various species assemblages, i.e., the malacological *Helicigona banathica* association characterizes the Eemian deposits of Germany (von Kolfschoten, 2000). This is specially reflected in the vertebrate fauna. As an example, *Hippopotamus, Stephanorhinus, Crocuta, Panthera, Bison* and/or *Paleoloxodon* remains, among others, are found in Central European interglacial deposits (Speelers, 2000; von Kolfschoten, 2000) and have allowed correlation of several Middle and Upper Pleistocene fluvial sequences (Schreve and Bridgland, 2002; Bridgland et al., 2004a,b; Bridgland and Westaway, 2008), specially from French, German and English rivers, made of either tufa or clastic sediments, but all formed during odd-numbered MIS.

Thus, it is noted that many rivers formed new terraces, which in some cases consist of tufa deposits, as in this study, during warm periods or cold-to-warm transitions. In contrast, they seemed to cut down and deepened their valleys following interglacial periods, which reflect responses driven by climate change, mainly at orbital (Milankovitch) frequencies (Bridgland et al., 2004a,b; Bridgland and Westaway, 2008). However, there are many other rivers with fewer terraces than these.

5. Conclusions

Here we have shown that ostracods are potential tools for amino acid racemization dating of tufa deposits. The aspartic acid and glutamic acid racemization ratios obtained in *H. reptans* valves provided the aminostratigraphy and aminochronology of tufa deposits located in central Spain linked to the Tagus river and some of its tributaries (the Henares, Dulce, Cifuentes, Ruguilla, Guadiela, Escabas and Trabaque rivers). Tufa accumulations were of diverse origin; while tufas from the Henares, Cifuentes and Ruguilla rivers were found to be of paludal origin, those from the Dulce and Tagus rivers were of fluviatile–paludal origin. The particular characteristics of the Henares, Cifuentes and Ruguilla rivers (infill of pre-existing valleys) implied that deposits of different ages were observed at the same elevation above the current river thalweg, and sometimes, older tufas were located below younger ones.

We distinguished eight main tufa-deposition episodes. These occurred predominantly during odd-numbered Marine Isotopic Stages, at 406 ± 90 (MIS 11), 264 ± 68 (MIS 7e), 189 ± 40 (MIS 7a), 130 ± 27 (MIS 6-5e), 101 ± 25 (MIS 5c), 32 ± 10 (MIS 3), 14 ± 4 (MIS 1), and 6 ± 2 (MIS 1) ka. These results are in agreement with the dating of similar deposits from nearby areas and other zones of Spain and Europe. Therefore, many large-scale river terrace sequences in Central Europe and Spain preserve sedimentary archives that appear to reflect fluvial system responses driven by climate change, i.e., while fluvial terraces formed during the temperate/warm interglacial periods and interstadial periods, downcutting occurred following these periods, under cold conditions.

The tufa stable-isotope compositions are similar to other examples in central and southern Spain and they plot in the same field as other lowland European stream tufas. The oxygen stable isotopes are interpreted to be influenced mainly by temperature and rainfall. The $\delta^{13}C$ values indicate a major influence of soil-derived carbon rather than the catchment area, but moderated in each tributary by the evaporation, flow regime (degassing processes) and biological effects (photosynthesis). It also appears that the $\delta^{13}C$ values do not depend on the age of the tufa deposits but on the study area since for a certain zone (e.g. Priego) the carbon isotopic content did not vary in samples of distinct age.

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